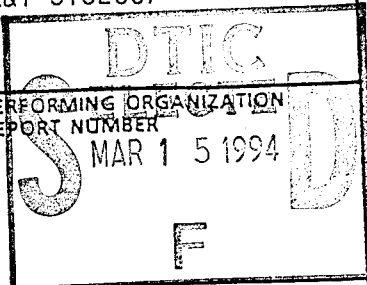


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Surface Studies of Poly(organophosphazenes) Containing Dimethylsiloxane Grafts

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ABSTRACT: Poly(organophosphazenes) containing dimethylsiloxane grafts were synthesized by carrying out hydrosilylation reactions on polymer precursors that contained unsaturated side groups. The surface properties of the siloxane-containing polymers were studied by contact angle measurements and X-ray photoelectron spectroscopy. A cosubstituent poly(organophosphazene) containing both trifluoroethoxy side groups and grafted dimethylsiloxane side groups was found to have a surface rich in $-CF_3$ groups. A poly(organophosphazene) with siloxane grafts but phenoxy groups as the second substituent showed surface enrichment of the siloxane species. Surface-specific hydrosilylation reactions were detected between an allyl-functional polymer and heptamethyltrisiloxane dissolved in non-solvents for the polymer. Polymer films showed the presence of silicon to depths of 25-60 μm as measured by energy dispersive X-ray spectroscopy.

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Introduction

A growing need exists for new polymer systems with predetermined surface properties. For example, the biocompatibility of a material is dependent on the nature of its surface and the interaction of that surface with living tissues^{1,2}. Platelet adhesion and blood coagulation are influenced both by the surface characteristics of a material and by the adsorption of serum protein on the surface. Adhesion is another property which is strongly surface-determined^{3,4}. The fundamental problem in polymer surface science is that a material with the required surface properties may not necessarily possess appropriate bulk properties, and vice versa. A solution to this dilemma is to select a polymer with the right combination of bulk properties and then develop methods to modify its surface.

Surface modification is not a new concept. Mechanical roughening, etching, and flame treatment have been used historically to alter the adhesive properties of a variety of materials, and surface coatings have long been used to improve the surface properties of a polymeric material. Recent work⁵⁻¹¹ has involved controlled chemical reactions carried out on the surface region or at the surface monolayer in order to functionalize and graft chemical species to that surface while, at the same time, leaving the bulk of the material unchanged.

Thus the ability to choose a polymer with desired bulk properties and to tailor its surface chemistry to suit a particular application has widespread consequences. The polyphosphazene family (**1**) is particularly suited to this approach. The macromolecular substitution route commonly used in poly(organophosphazene) synthesis^{12,13} allows control of the side group ratios, and this in turn influences the bulk and surface properties. Solubility, crystallinity, and mechanical properties may be varied within wide limits. In surface modification procedures, the high chemical stability of the P-N backbone often allows more aggressive chemical reactions to be carried out than with most polymers, with a lower likelihood of chain cleavage. Previous surface reactions of polyphosphazenes carried out in our program have included sulfonation¹⁴, hydrolysis¹⁵, oxidation¹⁶, and

nucleophilic substitutions¹⁷. Poly(organophosphazenes) have also been used as immobilization substrates for the covalent linkage of the enzymes, glucose-6-phosphate dehydrogenase and trypsin¹⁸.

Considerable interest exists in the preparation and examination of polymers which contain both organophosphazene and organosilyl units. A number of different synthesis routes have been investigated¹⁹⁻²⁹. Possible properties and uses for these materials include: low temperature elastomers^{19,20}, thermally stable or flame retardant materials^{21,22} and membranes with improved gas permeability²³. In this paper the focus is on the surface properties of poly(organophosphazenes) that contain siloxane grafts, and the surface-specific reactions of poly(organophosphazenes) via the hydrosilylation of unsaturated sites.

Results and Discussion

Surface Studies of Polymers Containing Siloxane Grafts The bulk properties of poly(organophosphazenes) that contain dimethylsiloxane grafts were described in an earlier publication²⁹. Here, the surface properties are of interest. Blends and copolymers of poly(dimethylsiloxane) (2) with organic polymers such as poly(methylmethacrylate), poly(vinylalcohol), and polysulfones have surfaces which are siloxane-rich, a consequence of the preferential migration to the polymer-air interface of the low surface energy, highly flexible dimethylsiloxane units³⁰⁻³³. The phase separation in block copolymers is determined by factors such as the copolymer composition, the flexibility of the block chain, and the interfacial tension between the copolymer chains³⁴. Surface migration of siloxane species is particularly important in applications where adhesion is to be minimized, since poly(dimethylsiloxane) generally forms very low intermolecular adhesive forces with other materials.

Polyphosphazenes with 4-allyloxyphenoxy side groups and either trifluoroethoxy (3) or phenoxy (4) cosubstituent groups were prepared. The allyl units were allowed to

react with heptamethyltrisiloxane in the presence of a platinum catalyst to give polymers with grafted dimethylsiloxane (**5** and **6**), as shown in Scheme 1. The single-substituent polymers, poly[bis(trifluoroethoxy)phosphazene] (**7**) and poly[bis(phenoxy)phosphazene] (**8**), were prepared for comparison. The compositions of the polymers used in the study are shown in Table 1. Polymer films were made by spin-casting solutions in THF onto glass slides. The surface properties of the polymers were then studied by contact angle measurements and by X-ray photoelectron spectroscopy (XPS). Contact angle measurements were obtained using a series of hydrocarbons and other organic liquids of known surface tension. These values were used to calculate the critical surface tension of wetting γ_c , which is a useful tool for the comparison of different surfaces and may aid the identification of the chemical groups present at a material surface. XPS data were collected at a takeoff angle of 35° , which corresponded to a penetration of approximately 50 Å into the polymer film. The results are shown in Tables 2 and 3 and Figure 1.

Tables 1-3, Scheme 1 and Figure 1 near here

Poly[bis(trifluoroethoxy)phosphazene] (**7**) was found to have a critical surface tension of approximately 16 mN/m. The surface energy is a fundamental thermodynamic property of a material, determined by the interactions of the atoms and molecules which make up the surface region. Low surface energies are a direct result of low intermolecular forces³⁵. The weakest interactions are London dispersion forces which are associated with aliphatic hydrocarbons and fluorocarbons. Among polymers, some of the lowest surface energy values result from surfaces of closely packed methyl groups (e.g. poly(dimethylsiloxane), $\gamma_c = 24$ mN/m³⁶) or aliphatic fluorocarbon pendant groups (e.g. poly(tetrafluoroethylene), $\gamma_c = 18$ -19 mN/m and poly(hexafluoropropylene), $\gamma_c = 16$ mN/m^{35,36}).

Poly[bis(trifluoroethoxy)phosphazene] has a glass transition temperature of -63°C . At room temperature sufficient polymer mobility exists to allow the surface-active $-\text{CF}_3$ unit to be presented to the surface. The experimentally determined critical surface tension value of 16 mN/m is similar to that of other fluoroalkyl polymers, and this strongly suggests that $-\text{CF}_3$ groups dominate at the surface. XPS data, on the other hand, show only a slight enrichment of fluorine over the theoretical bulk content. However, the XPS analysis depth of 50 \AA is perhaps too great to demonstrate the difference between surface and bulk compositions for this polymer, which has shorter side groups than the polymers which are discussed below. If the $-\text{CF}_3$ groups of poly[bis(trifluoroethoxy)phosphazene] are oriented towards the surface, with the $-\text{CH}_2\text{-O}-$ segments and the phosphazene backbone buried beneath, then the "surface region" might extend to a depth of about 5 \AA and not the 50 \AA which was actually sampled. XPS analysis of the top 50 \AA would therefore include too much of the bulk sample, with its random composition, for adequate characterization.

The contact angle values for polymer **5** were very similar to those of poly[bis(trifluoroethoxy)phosphazene] (**7**). Both polymers had γ_c values of approximately $16\text{--}17 \text{ mN/m}$. This suggests that the surface atomic composition of polymer **5** is very similar to that of poly[bis(trifluoroethoxy)phosphazene], even though the polymer contains a significant proportion of dimethylsiloxane units. Surface fluorine contents, determined by XPS, were higher than the theoretical composition. Carbon contents were lower, which is also consistent with a fluoroalkyl-rich surface, since the siloxane graft segment is richer in carbon than is the trifluoroethoxy segment. Taken together, the data from both surface techniques suggest that the trifluoroethoxy side groups migrate to the polymer-air surface in preference to the siloxane-containing groups. The driving force for polymer rearrangement is the minimization of the surface energy. Both polymer **5** and $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ have glass transition temperatures well below room temperature and it is assumed that the units in **5** are mobile at the evaluation temperature, which was $22\text{--}25^{\circ}\text{C}$. It seems reasonable

therefore to assume that polymer **5** rearranges into a configuration with -CF₃ units pointed toward the surface and the dimethylsiloxane segment buried more deeply in the bulk of the material.

Polymer **6** contains no trifluoroethoxy substituents. Here 80% of the side groups were phenoxy units and the remaining 20% contained siloxane grafts. Of the two types of side group, the siloxane-containing unit has a higher surface activity than the aromatic phenoxy group. Therefore it is not surprising that polymer **6** showed evidence of migration of the siloxane segments to the air interface. The XPS data showed the surface of **6** to be very low in nitrogen and phosphorus, while silicon was present at a much higher level than the theoretical value. This suggests that the P-N backbone is buried while the siloxane segments are oriented towards the surface. Contact angle data also support this interpretation. The critical surface tension of polymer **2** was calculated as 31 mN/m, which is much lower than that of the single substituent poly[bis(phenoxy)phosphazene], which was calculated to be 42 mN/m. For comparison, literature sources quote γ_c for PDMS as 24 mN/m³⁶.

All the polymers studied here are flexible elastomers that were above the glass transition at the temperature of testing. The flexibility of the polymers could allow the segments of lowest surface energy to preferentially orient towards the surface. In the case of polymer **5** this led to surface enrichment of the trifluoroethoxy group, while polymer **6** showed surface enrichment of the dimethylsiloxane graft. This is an interesting result, which demonstrates the relative surface active natures of the three types of substituent: trifluoroethoxy, dimethylsiloxane, and phenoxy. Therefore it is clear that the surface properties of multiple-substituent polyphosphazene materials will be affected most significantly by the substituent with the lowest surface energy, at least for those polymers which have the freedom to rearrange at a molecular level.

Contact angle data provide a convenient and useful way for characterization of the surface of a material, but problems can exist in the interpretation of the results. This is

particularly true with multiple component systems such as copolymers and cosubstituent polymers. Contact angle data values may vary as the polymer molecules take up different orientations in contact with different liquids at the surface. Contact angles are changed when the polymer surface is swelled by (or is dissolving in) the liquid being tested. In this work, the contact angles of hydrocarbon liquids on poly[bis(trifluoroethoxy)phosphazene] (7) and polymer 5 were steady, reproducible, and gave good Zisman plots. However, in the determination of γ_c for polymer 6 and poly[bis(phenoxy)phosphazene] (8), the contact angle data were not as reliable. Higher surface tension liquids were needed for the assessment, and many liquids showed interactions with the polymer surfaces. The experimentally determined γ_c values for these polymers may not be as accurate as those obtained for the other two.

Surface-Specific Modification of Polymers Containing Unsaturated Side Groups The allyl-functional polymer $[\text{NP}(\text{OCH}_2\text{CF}_3)_{1.46}(\text{OC}_6\text{H}_4\text{OCH}_2\text{CH}=\text{CH}_2)_{0.54}]_n$ (3) underwent a surface-specific hydrosilylation reaction under certain experimental conditions. Films of the polymer were immersed in a solution of heptamethyltrisiloxane in hexane, in the presence of a platinum catalyst. The exposure time was varied. The process was repeated using isopropanol as a solvent, instead of hexane. Both liquids are solvents for the siloxane reagent, but non-solvents for the polymer. The reaction was monitored by silicon analysis of the modified polymer, after a thorough washing process. Polymer cross-sections were examined by SEM with energy dispersive X-ray spectroscopic analysis. The reaction conditions and analysis results are shown in Table 4.

It was important in this study to prepare and analyze suitable reference samples, to confirm that unreacted siloxane species were removed in the washing process. Reference polymer films were exposed to heptamethyltrisiloxane solutions without the platinum catalyst. In the absence of the catalyst, no reaction was expected (and none was detected).

Reference samples **e** and **f** (hexane), and **h** (isopropanol) did not show any significant increase in silicon content over the background values. Since silicon was not detected in the reference samples, it seems reasonable to assume that the silicon detected in the surface regions of **d** and **g** resulted from siloxane grafting reactions instead of just mixing.

Analysis of a point in the surface region of sample **d** showed a significant silicon content. A point in the center of the sample showed a silicon level comparable to the background value. Thus, it was possible to generate a profile map which showed not only a significant increase in Si content at both surface regions, but allowed the reaction depth to be measured. Sample **d**, which was treated for 24 hours in a hexane solution of heptamethyltrisiloxane, showed a penetration of 35-60 μm . Sample **g**, treated for 24 hours in an isopropanol solution, showed significant surface enrichment of silicon to a depth of 25-30 μm . Analysis profiles and X-ray elemental analysis count rate spectra are shown in Figures 2-4.

Experimental Section

Instrumentation. NMR spectra were obtained using a Bruker WP-360 MHz NMR spectrometer, with ^{31}P chemical shifts referenced to aqueous phosphoric acid.

Differential scanning calorimetry was carried out using Perkin-Elmer DSC-7 equipment. Samples (10-15 mg) were heated within an atmosphere of dry nitrogen in aluminum pans, with an empty aluminum pan as reference. The heating rate was $20^{\circ}\text{C}/\text{min}$.

Electron microscopy was performed at the Electron Microscope facility for the Life Sciences in the Biotechnology Institute at the Pennsylvania State University. Energy dispersive X-ray spectroscopy was carried out using a PGT IMIX version 7 X-ray analyzer attached to a JEOL JSM 5400 scanning electron microscope. Polymer films were fractured after dipping in liquid nitrogen. Smooth fracture surfaces were obtained. The film pieces were mounted edge-on onto aluminum stubs using conducting adhesive, and were coated with carbon using a BAL-TEC SCD 050 sputter-coater. Samples were scanned using an accelerating voltage of 20 kV at an angle of 30° .

Starting Materials. Poly(dichlorophosphazene) was synthesized by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene at 250°C ³⁰. Hexachlorocyclotriphosphazene (provided by Ethyl Corp.) was purified by two recrystallizations from hexane and two vacuum sublimations. Phenol (Aldrich) was dried by azeotropic removal of water by benzene and was further purified by vacuum sublimation. Poly(dichlorophosphazene), sodium, and sodium hydride were stored and handled in a nitrogen filled glove box. 2,2,2-Trifluoroethanol was treated with sodium carbonate and distilled before use. Tetrahydrofuran and dioxane were freshly distilled from sodium benzophenone ketyl. All reactions were carried out under a stream of dry argon using standard Schlenk techniques.

Heptamethyltrisiloxane (Petrarch) was distilled and stored under dry argon. Tetramethyl-1,3-divinyl disiloxane platinum complex (Petrarch) was used as received. 4-

Allyloxyphenol was prepared by the reaction of hydroquinone with allyl bromide, as described previously²⁹.

Synthesis of Polymers. Polymers with varying ratios of allyl-functional side groups and either trifluoroethoxy or phenoxy cosubstituent groups were prepared by the nucleophilic replacement of chlorine in poly(dichlorophosphazene) by the sodium alkoxide and/or aryloxide. The reaction conditions and purification procedures have been described in earlier work²⁹. Polymers with unsaturated side groups were synthesized, purified and modified by hydrosilylation reactions (Scheme 1). ¹H NMR assignments for the unsaturated substituent groups were: δ 7.7-6.6 (broad d, Ph), δ 6.0 (s, -CH=), δ 5.3 (d, =CH₂), δ 4.2 (s, -OCH₂). Protons assigned to trifluoroethoxy and phenoxy substituents were detected at δ 4.6-4.0 and δ 7.1-6.8 respectively. ¹H NMR assignments for the siloxane-containing substituent groups were: δ 7.7-6.6 (broad d, Ph), δ 3.9 (s, -OCH₂), δ 1.9 (s, -CH₂-), δ 0.7 (s, -CH₂Si), δ 0.1 (broad m, SiCH₃).

Surface-Specific Hydrosilylation Reactions. A 2.0 g sample of purified polymer **3**, [NP(OCH₂CF₃)_{1.46}(OC₆H₄OCH₂CH=CH₂)_{0.54}]_n was dissolved in 10 mL of THF. The viscous solution was cast onto a Teflon sheet-coated mold. The film was allowed to dry for 3 days in a THF-enriched atmosphere and for a further 8 hours under vacuum. The free-standing polymer film was cut into strips of approximate dimensions 10 mm x 20 mm x 400 μ m. These films were exposed to heptamethyltrisiloxane dissolved in liquids which were non-solvents for the polymer. The aim was to obtain surface-specific modification of the unsaturated polymer samples. Several different sets of reaction conditions were chosen. Six polymer films were immersed in a solution containing 3.5 g heptamethyltrisiloxane and 100 mL hexane, for varying periods of time both with and without the addition of 20 mg tetramethyl-1,3-divinyl disiloxane platinum complex. The same process was repeated, substituting 100 mL isopropanol for hexane. All samples were agitated vigorously during the treatment using a mechanical shaker. After the specified length of time the samples were removed from the siloxane solutions and an extensive

washing process was carried out. Each sample was washed a total of 12 times with either hexane or isopropanol (the liquid corresponding to the reaction medium) with vigorous agitation (8 times), sonication (twice) and soaking periods of 16 hours each (twice). Extensive washing ensured that any unreacted, entrapped heptamethyltrisiloxane was removed before analysis for silicon.

Surface Analysis. Smooth polymer films were obtained by spin casting THF solutions onto clean glass microscope slides at a speed of 2000 rpm. Contact angle measurements were obtained using a traveling microscope fitted with a Rame-Hart goniometer eyepiece. The contact angle liquids (Aldrich) were all distilled under dry argon gas immediately before use, except for glycerol which was used as received. Liquid drops were placed by means of a Gilmont syringe and a 24-gauge flat-tipped needle, inside an environmental chamber saturated with the vapor of the liquid in use. Contact angles were reported as the average of measurements taken from both sides of ten liquid drops, where measurements were taken within 15 seconds of application. Values of the critical surface tension of wetting, γ_c were obtained by extrapolation of surface tension to $\cos \theta = 1$ for the plot of $\cos \theta$ against liquid surface tension.

X-ray photoelectron spectroscopy was carried out using a takeoff angle of 35° , giving an approximate analysis depth of 50 Å into the polymer matrix.

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Table 1. Polymer Compositions and Glass Transition Temperatures

polymer	polymer structure	T _g (°C) ^a
5	[NP(OCH ₂ CF ₃) _{1.46} (OC ₆ H ₄ O{CH ₂ } ₃ SiMe ₂ OSiMe ₂ OSiMe ₃) _{0.54}] _n	-62
6	[NP(OC ₆ H ₅) _{1.60} (OC ₆ H ₄ (CH ₂) ₃ SiMe ₂ OSiMe ₂ OSiMe ₃) _{0.40}] _n	-17
7	[NP(OCH ₂ CF ₃) ₂] _n	-63
8	[NP(OC ₆ H ₅) ₂] _n	-8

^a Glass transition temperatures were determined by DSC at a heating rate of 20°C/min.

Table 2. Contact Angle Data

γ_l (mN/m)	contact angle in degrees (cosine in parentheses)			
	polymer 5	polymer 6	polymer 7	polymer 8
18.4	28.8 (0.876)	b	26.3 (0.896)	b
20.3	35.6 (0.813)	b	38.4 (0.784)	b
21.8	41.7 (0.747)	b	41.3 (0.751)	b
23.0	47.1 (0.681)	b	46.7 (0.686)	b
23.9	52.3 (0.612)	b	53.0 (0.602)	a
25.4	57.3 (0.540)	35.8 (0.811)	57.1 (0.543)	a
26.7	60.1 (0.498)	33.4 (0.835)	60.3 (0.495)	a
27.0	62.6 (0.460)	36.8 (0.801)	62.8 (0.457)	a
27.6	63.1 (0.452)	36.6 (0.803)	63.3 (0.449)	a
28.1	63.8 (0.442)	28.0 (0.883)	65.9 (0.408)	a
32.1	-	22 ^c (0.927)	-	a
36.0	-	29.8 (0.868)	-	a
39.8	-	85.4 (0.802)	-	a
44.6	-	50.4 (0.637)	-	31 ^c (0.857)
50.8	-	82.0 (0.139)	-	39.9 (0.767)
58.2	-	102.1 (-0.210)	-	70.4 (0.335)
63.4	-	112.8 (-0.388)	-	74.6 (0.266)
73.1	-	120 ^c (-0.500)	-	92.4 (-0.042)

The liquids used in this study, in order of increasing surface tension, were: hexane, heptane, octane, nonane, decane, dodecane, tetradecane, pentadecane, hexadecane, heptadecane, styrene, hexachloro-1,3-butadiene, acetophenone, 1-bromonaphthalene, diiodomethane, formamide, glycerol, and water. Surface tension values were obtained from published data^{37,38}.

^a These liquids caused swelling of the polymer surface. Contact angle data did not fit the Zisman plot.

^b These liquids spread across the polymer surface.

^c These values are approximate due to variations in the measured contact angle.

Table 3. Surface Composition of Polymer Films by XPS Analysis

element	composition in atomic percentages					
	polymer 5		polymer 6		polymer 7	
carbon	29.1	(46.2)	52.8	(71.4)	25.1	(28.6)
oxygen	16.7	(15.4)	24.4	(14.3)	13.1	(14.3)
nitrogen	5.1	(4.8)	0.5	(4.5)	5.9	(7.1)
phosphorus	5.5	(4.8)	0.8	(4.5)	6.9	(7.1)
silicon	5.1	(5.8)	21.5	(5.4)	0.0	(0.0)
fluorine	38.4	(23.1)	0.0	(0.0)	48.6	(42.9)
total	99.9	(100.1)	100.0	(100.1)	99.6 ^a	(100.0)

Theoretical atomic percentages, shown in brackets, were calculated by assuming an even distribution of all elements, excluding hydrogen which was not detected.

^a The remaining 0.4% was detected as sodium.

Table 4 Surface Treatment of Polymer 3

sample	reaction medium	catalyst	reaction time	silicon analysis
a	hexane	Pt	30 minutes	no Si detected
b	hexane	Pt	2 hours	no Si detected
c	hexane	Pt	6 hours	Si detected at low levels
d	hexane	Pt	24 hours	Si detected to a depth of 60 μm
e	hexane	none	2 hours	no Si detected
f	hexane	none	24 hours	no Si detected
g	isopropanol	Pt	24 hours	Si detected to a depth of 30 μm
h	isopropanol	none	24 hours	no Si detected

CAPTIONS TO FIGURES

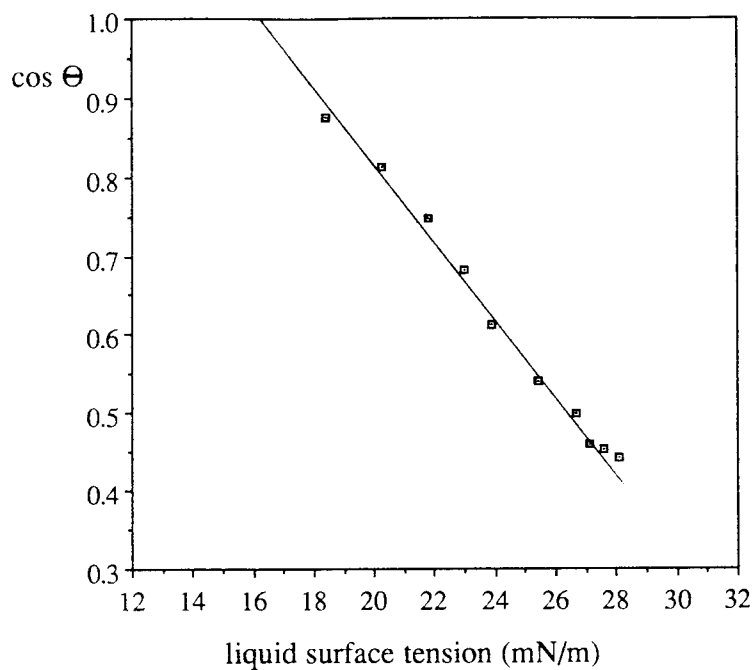
Figure 1. Zisman plots for polymers **5-8**. γ_c values were determined by extrapolation to $\cos \Theta = 1$.

Figure 2. X-ray spectra of reference samples **e**, **f**, and **h**. Only phosphorus was detected at significant levels.

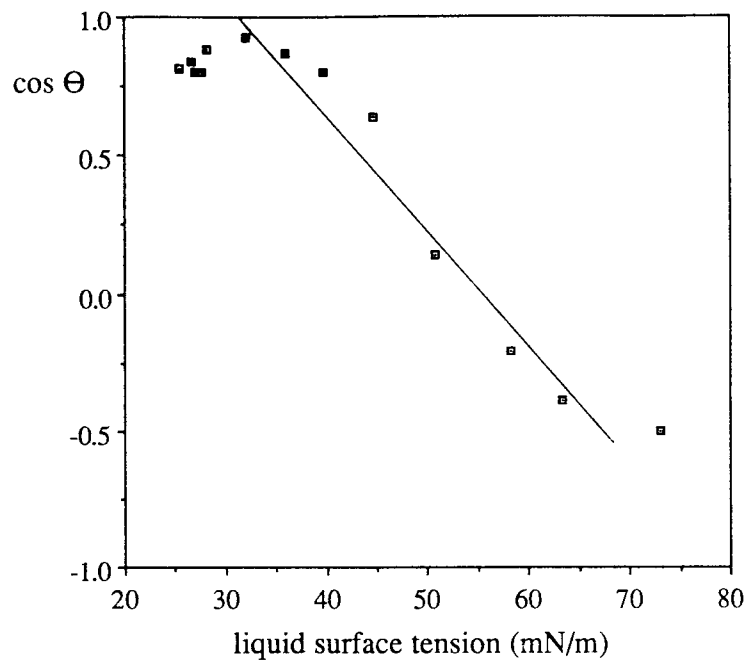
Figure 3. Cross-section of sample **d**. The sample surface is visible as a light region towards the left of the photomicrograph. The silicon line profile analysis of the cross-section shows increased Si levels to a depth of approximately 60 μm at both surfaces. The X-ray spectrum obtained in the surface region showed both silicon and phosphorus.

Figure 4. Cross-section of sample **g**, showing silicon and phosphorus line profile analyses. Phosphorus levels did not vary significantly across the sample cross-section. Silicon levels were increased in both upper and lower surface regions.

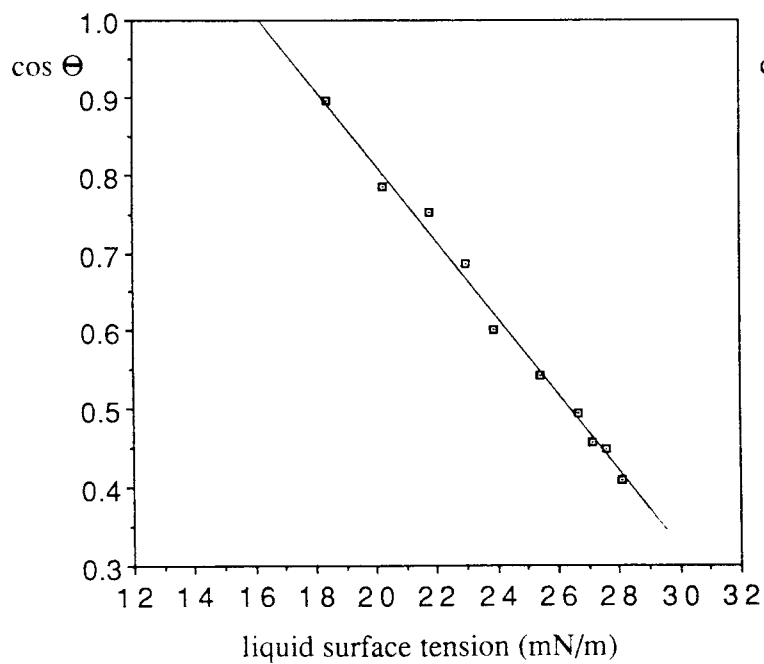
5 $\gamma_c = 16 \text{ mN/m}$



6 $\gamma_c = 31 \text{ mN/m}$



7 $\gamma_c = 16 \text{ mN/m}$



8 $\gamma_c = 42 \text{ mN/m}$

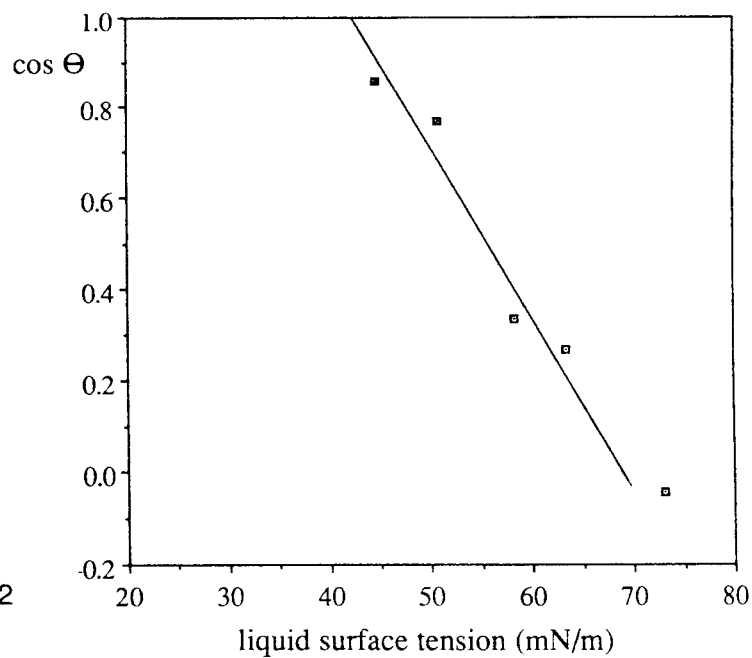


Figure 1

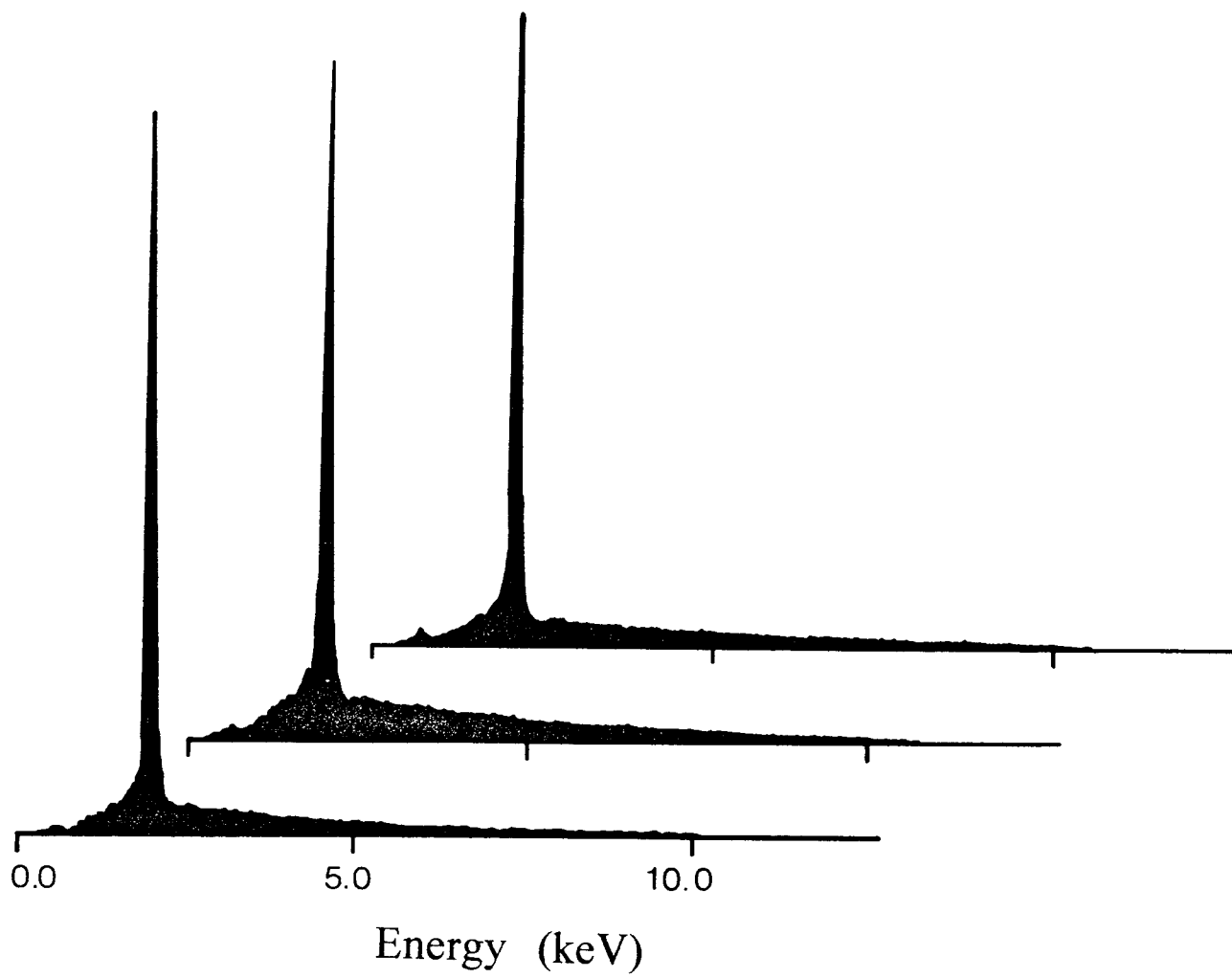


Figure 2

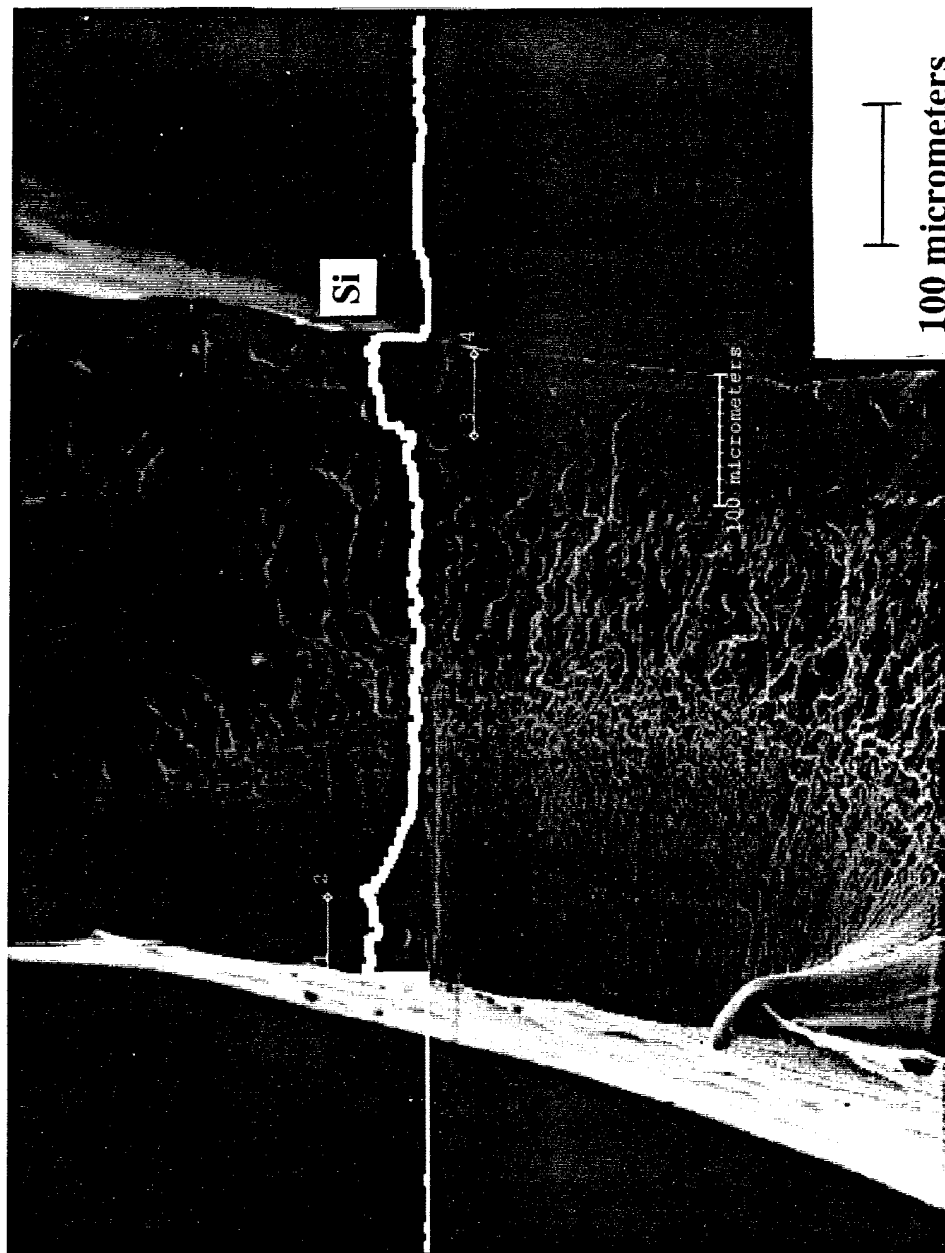


Figure 3

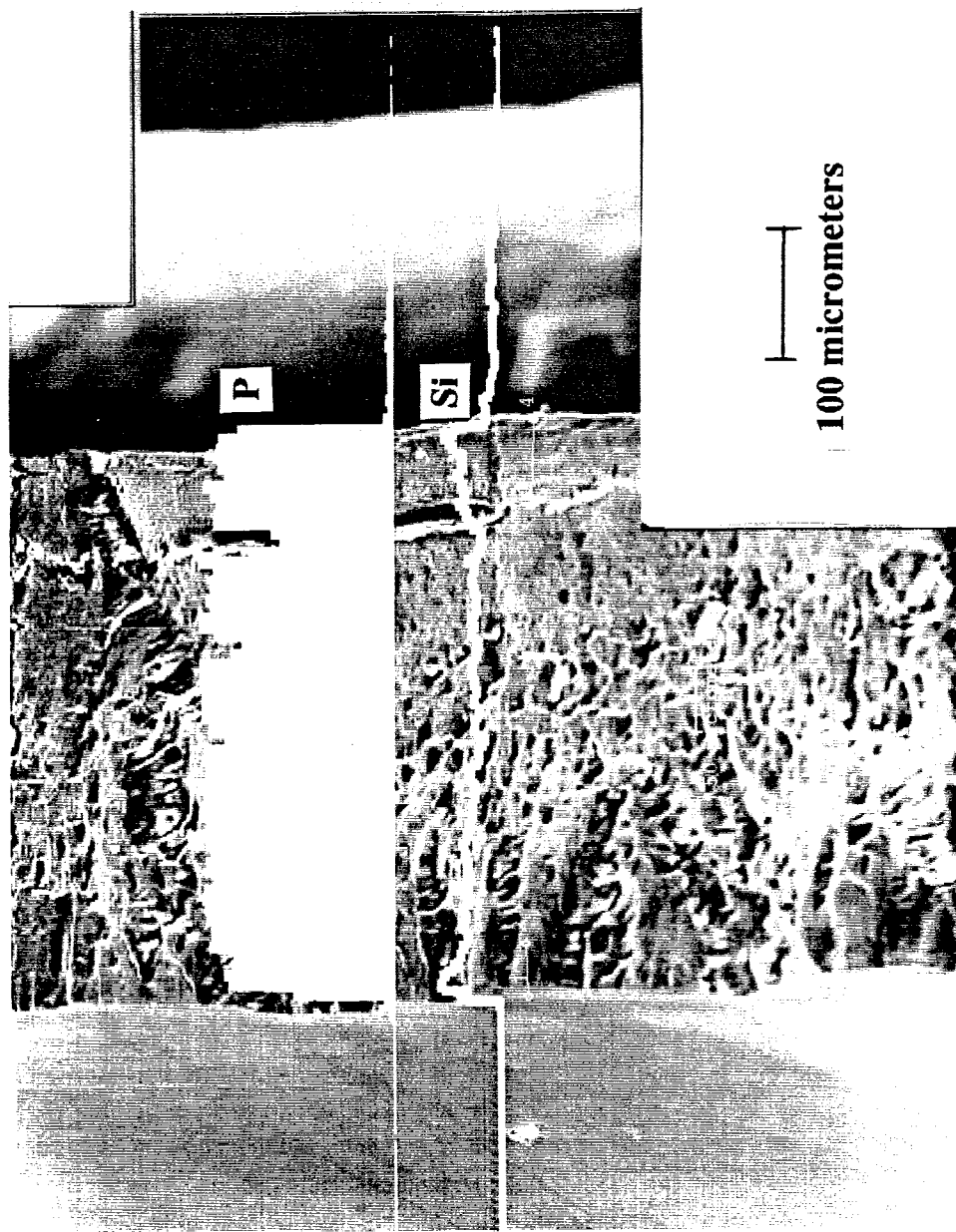
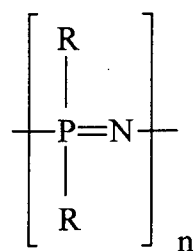
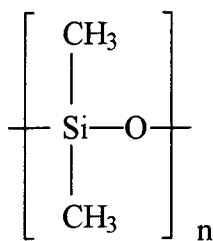


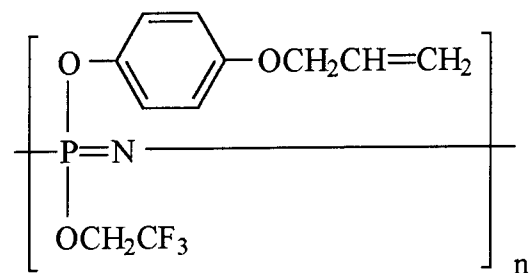
Figure 4



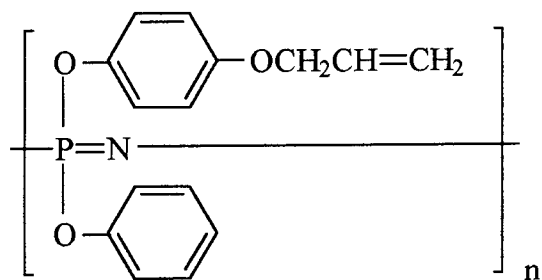
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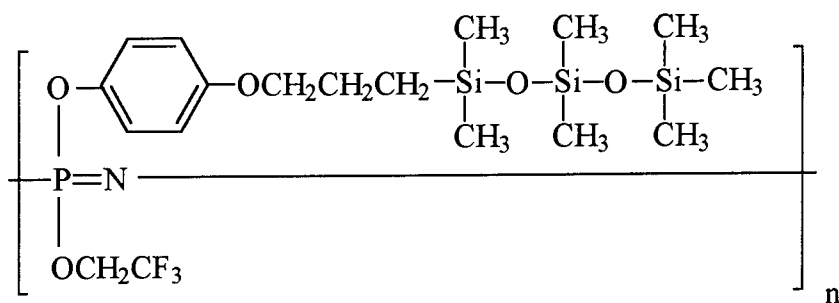
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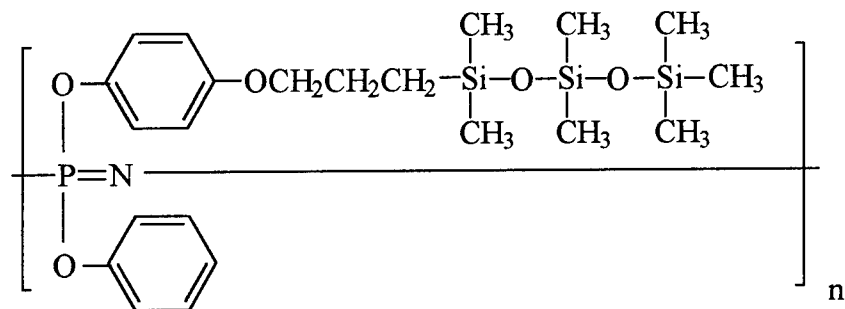
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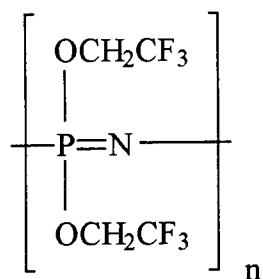
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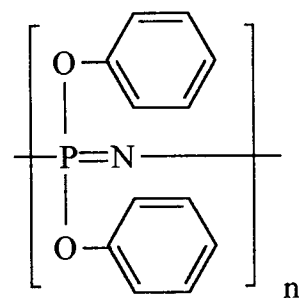
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